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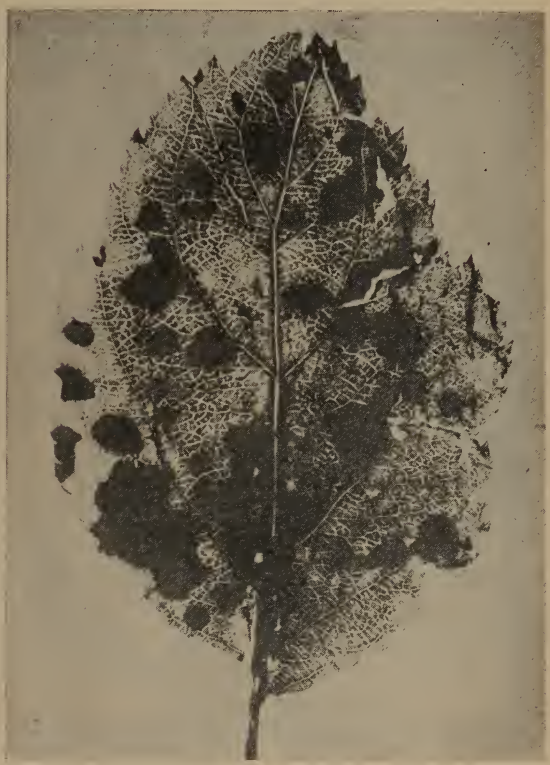
COLLEGE OF AGRICULTURE.

AGRICULTURAL EXPERIMENT STATION.

ARSENICAL INSECTICIDES.

PARIS GREEN; COMMERCIAL SUBSTITUTES; HOME-MADE ARSENICALS.

By GEO. E. COLBY.



APPLE LEAF "BURNED" BY PARIS GREEN.

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ARSENICAL INSECTICIDES.

At the present time there are used in the United States for horticultural purposes from 1,500 to 2,000 tons of paris green annually, and the enormous increase in the demand has caused manufacturers to put upon the market products which have been carelessly or hastily manufactured.

"White arsenic" is used in the manufacture of paris green, and it is not an uncommon practice to use needless and excessive amounts; while on the other hand the finished product is often lower in total arsenic than is lawful in the State where made, and then is strengthened by the addition of more "white arsenic" (arsenious oxid). Thus, paris green, which at best is a somewhat variable compound, comes by these abuses to contain much free arsenious oxid, which in spraying materials is ready and certain to injure and destroy foliage.

The application of compounds carrying any water-soluble leaf-destroying matter is particularly dangerous in semi-arid climates. Horticulturists in California have learned from experience that arsenical spraying materials are often unreliable and dangerous, and for years have been sending samples of their purchases of paris green to this Station for examination as to purity, there being no simple and easy chemical test by which one who is not a chemist can satisfactorily determine the presence of "white arsenic" in a material. Inasmuch as the State of California has by law fixed the maximum quantity of "white arsenic" in paris green for insecticide purposes at four per cent, and requires an analysis to be made by this Station and a certificate thereof given to the importer or dealer, it rests wholly with the orchardist whether he uses safe material or not on his fruit trees. When buying paris green the farmer may now demand to be shown a copy of the certificate before purchasing; and he may even have the particular parcel which constitutes his purchase examined by sending a fair sample to the Station in Berkeley.

Pure Paris Green, also called Emerald green, Schweinfurt green in Europe, is an aceto-arsenite of copper, and may be regarded as a compound of *verdigris* and *Scheele's green* (arsenite of copper), having this percentage composition: Copper oxid (CuO), 31.29; Arsenious oxid (As_2O_3), 58.65; and Acetic acid ($C_2H_4O_2$), 10.06 (Report of N. J. Agricultural Experiment Station, 1897, p. 408); in other words, it is a compound made by the union of three substances—copper oxid, arsenious oxid, and a little acetic acid. Ordinary commercial paris green contains, besides a very little moisture, some sodium sulfate or glauber salt. This salt usually occurs to the extent of 1 or 2 per cent, because it has not been fully washed out in the process of manufacture. In the tables of analyses of paris green, given farther along, we have reported the

usual amount by the word "small," and excessive quantities by the word "large," under the head of *sodium sulfate*. This compound is of no value as an insecticide: it must be classed as a "make-weight," and causes the buyer to pay a very high price (ten times more than its value) for every part of paris green which it replaces.

While from this or any ordinary description of pure paris green it might appear to be a very simple matter to make it, in reality its manufacture is difficult, even when effected according to the latest "instantaneous" process. Many chemicals enter into the process, which must be put together in the right proportions, and at just the right time; requiring, besides experience, various kinds of appliances and machinery, "striking-tanks," crushing, sifting, or bolting apparatus—all of which is quite beyond the reach of any one individual.

Physical Condition of Paris Green.—The best paris green is a powder composed of crystalline globules of microscopic fineness; and unless the particles are fine enough to pass through at least a 100-mesh sieve the green should be condemned as unfit for spraying purposes; for with a green in which larger particles appear there is no chance for an even distribution of the poison. The aggregation of globules is probably brought about by careless grinding and bolting, or perhaps by the after-treatment with water given to take away impurities. In drying from this operation the globules cohere and form strings and bunches of particles of green, which are sometimes found also to be bound together by large lustrous crystals of uncombined "white arsenic." This latter condition is, of course, very objectionable, but easy to determine.

But whatever property paris green possesses, one essential quality of the pure article, in so far as the intent and purposes of spraying operations are concerned, is that all of the arsenic in it must be combined with copper so that it may be insoluble in pure water. This is true, no matter what may be claimed by some chemists as to its solubility, for conditions in the laboratory are variable and do not obtain in the practical use of paris green in the field.

WORK ON PARIS GREEN AT THIS STATION.

The following statement gives the character of the work done on paris green at this Station during the years 1899, 1900, 1901, and 1902:

Before the session of the Legislature of 1901, this Station examined thirty-seven samples of paris green, and it was found, and so reported, that only 22 per cent were acceptable for use in California orchards, according to its standard (p. 17, Cala. Stat. Bull. 126).

The results of this work have been useful not only in establishing the fact that manufacturers can and readily do produce paris greens that will not injure the leaves of the delicate peach or other deciduous trees, even in the arid region, but also in the introduction of a more improved and rational method of analysis, which has been accepted by the chemists of the States whose results had previously very frequently contradicted ours. As early as the spraying season of 1901, a number of the largest manufacturers began to make a paris green marked by a

separate "poster" on each package as "paris green specially prepared to conform to the requirements of the Agricultural Experiment Station of California, as suggested in their Bulletin No. 126." These brands were, on examination, found to conform to the California standard; and before the spraying season of 1902 some manufacturers were offering to the horticulturists of other States materials that had been sent to this Station for judgment as to their purity.

At the session (1901) of the Legislature a law was passed which fixed the maximum permissible content of free arsenious oxid ("white arsenic") at *four* (4) per cent, and the minimum of total arsenious oxid in paris green at fifty (50) per cent. This was the first law in the United States which fixed the *maximum quantity of "white arsenic" permissible in paris green;* other State laws simply governed the total amount of the poison. In pursuance of this law samples representing 19 tons (of 2,000 pounds each) have been experted, and only five tons (about 26 per cent) have been condemned by not having a certificate of purity issued from this office according to the provision of the law.

Twenty-five tons is about the normal quantity of paris green used on the Pacific Coast, and of this amount California must have had its fair share last year, for in addition to the 19 tons examined there was much in stock whose weight was not given by some dealers who had failed to receive a certificate. Besides those from the dealers or jobbers, about fifty other samples from individual horticulturists have been examined.

The paris greens in the tables which follow are classified in two groups, viz.: (1st) Those examined here before the California law governing the sale of paris green went into effect; (2d) Those examined after the law went into effect. Both these groups are, for the ease of determining the quality of the articles, again subdivided into *satisfactory* and *objectionable* articles.

In the *first group* only one fifth were satisfactory in composition, and only two out of eight were received from orchardists. Of the objectionable articles of this class or group over one half (sixteen out of twenty nine) were received from farmers, the rest coming from dealers.

In the *second group*, or those received since the law took effect, forty-six were satisfactory and forty-five were objectionable. Of the satisfactory ones one half came from the dealers and the remainder from the orchardists, but some of those from the dealers are described as being "only advance samples" for examination from lots ordered or about to be ordered from Eastern makers.

Of the *objectionable ones* of the *second group*, fifteen out of forty-five are from the dealers; private parties having, according to their statements, sent in "left-over" greens which they wished analyzed after having learned that a law had been enacted. In any event, it is seen that the satisfactory samples just equal in number the objectionable ones of this group. So on the whole it appears that the orchardists were immediately benefited by the enactment of the paris-green law. Most of the dealers have assisted to hasten this right condition of the market as regards the *quality* of the material which they have handled.

TABLE SHOWING RESULTS OF THE EXAMINATION OF PARIS GREEN.

Samples received *before* the California law went into effect (Feb. 28, 1901).

Number.	Sender.	Manufacturer.	Microscopic Examination. (After washing out the white arsenic no projecting crystals were left in any sample.)		Chemical Examination.			Remarks.
			Projecting Crystals of White Arsenic.	Other Appearances.	Arsenious Oxid. Total.	Arsenious Oxid. Water-Soluble White Arsenic.	Sulfate of Soda. (Glauber Salt.)	
	Satisfactory.							
498		Unknown			54.10	3.50	small	
499		Unknown				4.10	small	
527	Acme Color Works	Acme Color Works	few		50.15	3.81	small	
532	Mack & Co.	Ansbacher & Co.	many	Many loose octahedrons and broken-down green		3.95	excessive	
536	Adler Color Works	Adler Color Works	almost none			2.80	small	
537	Adler Color Works	Adler Color Works	almost none			2.97	small	
540	Adler Color Works	Adler Color Works	some	Few octahedrons and much broken-down green		4.09	small	
542	F. L. Lavanburg	F. L. Lavanburg	very little			3.10	small	
	Objectionable.							*Copper Oxid.*
500	B. M. Lelong	Unknown	few		48.97	6.70	excessive	27.93
501	J. D. Cuthbert	Unknown	many		48.27	8.10	excessive	28.06
502	T. G. Phelps	Unknown	studding the green		52.90	29.40	excessive	32.60
503	Mack & Co.	Unknown	studding the green		55.63	24.00	excessive	
504	F. A. Little	Unknown	many		57.78	9.10	normal	34.60
505	Mack & Co.	Unknown	studding the green		52.90	23.60	small	31.25
511	B. M. Lelong	Unknown	many			18.32	large	
512	W. P. Fuller & Co.	Unknown	many			8.53	trace	
513	A. Block	Unknown	many			9.70	considerable	
514	Langley & Michaels Co.	Unknown	studding the green			large	large	
515	W. P. Fuller & Co.	Unknown	many			9.50	large	
516	Fabian Joost	Unknown	many			7.92	large	
518	Alden Anderson	Unknown	few				small	
519	P. Van Löben Sels	Unknown	many				excessive	

520	P. Van Löben Sels	Unknown	not many				small
521	P. Van Löben Sels	Unknown	not many				excessive
522	J. J. January	Unknown	many large			17.40	small
523	Langley & Michaels Co.	Unknown	many small			12.40	small
524	T. H. Goodman	Unknown	many			16.30	excessive
525	J. R. Fontain	Unknown	many			15.80	excessive
526	Chas. Ford Co.	Unknown	very large			25.00	small
528	John Murphy	Unknown	rather large			16.50	excessive
529	John Lucas Co.	F. L. Lavanburg	many fine			6.36	small
530	John Lucas Co.	F. L. Lavanburg	many			11.62	small
531	John Lucas Co.	Unknown	many			9.96	small
533	C. G. Poirier	Unknown	some	Octahedrons		6.43	excessive
538	Fred L. Lavanburg	F. L. Lavanburg	some			8.90	excessive
539	W. P. Fuller & Co.	Acme Color Works	some			8.43	small
541	Kirk, Geary & Co.	Unknown	some	Octahedrons and broken-down green		4.14	small

TABLE SHOWING RESULTS OF THE EXAMINATION OF PARIS GREEN—*Continued.*

Samples received *after* the California law went into effect (Feb. 28, 1901).

Number	Sender, Brand, Etc.	Manufacturer.	Microscopic Examination of Sample as Received. (After washing out the free arsenic no projecting crystals were left in any sample.)		Chemical Analysis.			Amount Represented.
			Projecting Crystals of White Arsenic.	Other Appearances.	Total Arsenious Oxid.	Free Arsenious Oxid. *White Arsenic.*	Sulfate of Sodium. (Glauber Salt.)	
	Satisfactory.							
543	Kirk, Geary & Co.	Adler Color Works, New York	little	Much br'ken-down green		2.9	small	1,915 pounds.
569	Langley & Michaels Co.	Adler Color Works, New York	little		52.12	3.8	small	3,250 pounds.
581	Robert Lamont	Adler Color Works, New York	few				small	
580	F. L. Lavanburg	Atlantic Color Works, N. Y.	few				small	* 1 pound.
583	Langley & Michaels Co.	Adler Color Works, New York	few		55.50	1.70	small	1,020 pounds.
584	W. P. Fuller & Co.	A. B. Ansbacher, New York	small		58.47	3.20	small	3,168 pounds.
585	F. W. Braun & Co.	F. L. Lavanburg, New York	small		58.75	3.93	small	200 pounds.
590	Langley & Michaels Co.	Atlantic Color Works, N. Y.	few		59.37	3.50	small	1,200 pounds.
591	C. H. Rodgers (Fuller & Co.)	A. B. Ansbacher, New York	few			3.95	small	
592	C. H. Rodgers (Langley &	Michaels Co.)	few			3.10	small	
598	Langley & Michaels Co.	Adler Color Works, New York	few	Much br'ken-down green	58.00	2.30	small	
599	Redington & Co.	Adler Color Works, New York	few	Much br'ken-down green	58.00	2.20	small	980 pounds.
600	Redington & Co.	Atlantic Color Works, N. Y.	very few			2.60	small	5 lbs. adv'nce sample.
601	Adler Color Works		few small	Few octahedrons		1.80	small	1 lb. advance sample.
602	Adler Color Works		few small			1.69	small	1 lb. advance sample.
603	Mack & Co.	A. B. Ansbacher, New York	few small		58.00	2.30	small	1 lb. advance sample.
604	W. P. Fuller Co.	A. B. Ansbacher, New York	few small			2.00	small	1 lb. advance sample.
605	Geo. Z. Wait	Lehn & Fink		Few octahedrons		2.30	small	1 lb. advance sample.
607	Anne Color Works		few			3.20	small	1 lb. advance sample.
608	W. P. Fuller & Co.	A. B. Ansbacher, New York	few		58.10	2.20	small	5,359 pounds.
609	Mack & Co.	A. B. Ansbacher, New York	few		60.00	1.80	small	6,039 pounds.
610	Redington & Co.	F. L. Lavanburg, New York	few		58.70	2.00	small	3,040 pounds.
611	Geo. Z. Wait	Lehn & Fink	few		58.00	3.10	small	2,080 pounds.
612	Geo. H. Cutter		very few				large	½ ounce.
614	J. J. Keegan		few		58.75	2.90	small	1 ounce.

615	A. Plumley		few	Few octahedrons			large	½ ounce.
616	R. C. Kells		few		59.1	2.50	small	½ ounce.
617	C. J. Moore		few			1.70	small	homo. vial.
618	Western Wholesale Drug Co., Los Angeles.		few	Much br'ken-down green	61.0	3.78	small	400 pounds.
619	Woodward Bros.		few	Few octahedrons	60.0	2.70	small	½ ounce.
621	C. C. Councilman		some	Some octahedrons		2.40	small	1 ounce.
623	A. V. Stubenrauch		small	Few octahedrons	59.43	2.50	small	2 ounces.
624	J. H. B. Pilkington		few			2.40	small	2 ounces.
625	B. W. Borchers		few			3.40	small	1 ounce.
626	J. D. Murphy		few			2.70	small	1 ounce.
627	William Swall		few			2.10	small	1 ounce.
628	A. Hoyt		small	Br'ken-down green		3.10	small	3 ounces.
629	H. H. Whitman		few			2.30	small	1 ounce.
630	I. F. Adams		few			2.20	small	2 ounces.
633	C. H. Squire, "Horticultural Brand"	A. B. Ansbacher, New York	very few		60.33	2.90	small	4 ounces.
634	Mack & Co.	A. B. Ansbacher, New York	few small		60.00	2.70	small	3,650 pounds.
635	W. P. Fuller & Co., "Horticultural Brand"	A. B. Ansbacher, New York	few	Few octahedrons	60.00	2.90	small	3,166 pounds.
636	J. H. B. Pilkington		few			3.70	large	1 ounce.
637	J. A. Scholefield		many	Some octahedrons		3.70	large	1 ounce.
638	Langley & Michaels Co.	Adler Color and Chemical Works, New York	few	Few octahedrons	59.16	2.20	small	2,340 pounds.
639	J. F. Latman		few			3.40	large	1 ounce.

* Said to represent output of works.

TABLE SHOWING RESULTS OF EXAMINATION OF PARIS GREEN—*Continued.*

Samples received *after* the California law went into effect (Feb. 28, 1301).

Number	Sender.	Manufacturer.	Microscopic Examination.		Chemical Examination.			Amount Represented.
			Projecting Crystals of White Arsenic on the Green.	Other Appearances.	Arsenious Oxid. Total.	Arsenious Oxid. Water-Soluble White Arsenic.	Sulfate of Soda. (Glauber Salt.)	
	Objectionable.							
544	A. E. Burnham	Unknown	considerable			7.50	excessive	
545	William Hunter	Unknown	some			12.30	excessive	
546	William Hunter	Unknown	some			8.30	small	
547	Alden Anderson	Unknown	some			7.90	small	
548	Felix Foreman	Unknown	some			10.30	excessive	unsafe.
549	Felix Foreman	Unknown	some			9.70	excessive	unsafe.
550	Fred. Foster	Unknown	on each sphere		51.16	11.30	large	85 lbs. left over.
551	Geo. Z. Wait	Lehn & Fink	much	Much br'ken-down green	47.73	8.20	large	
552	Mack & Co. (Codlin Brand)	A. B. Ansbacher	studding the green	Few octahedrons	51.76	14.80	large	
554	E. O. Webb	Unknown	some	Octahedrons	50.28	7.30	large	56 pounds.
555	J. R. Smith	Unknown	few			small	small	
556	F. L. Monnet	Unknown	binds the green				excessive	
557	W. Donald & Co. (Star Brand)	F. L. Lavanburg	binds the green		51.54	15.20	excessive	
558	W. J. Westlake	Unknown	suspicious					
559	Farmers' Union	Unknown	studding the green		50.28	24.00	excessive	
560	W. B. Whitney	A. B. Ansbacher	studding the green		51.60	10.30	small	
561	H. F. Clark	Unknown	many remnants					too coarse.
562	Yates & Co.	A. B. Ansbacher	much		50.91	9.20	excessive	
563	L. A. Walton	Unknown	small crystals					too coarse.
564	Meek Estate	Unknown	binds the green					
565	Redington & Co.	Acme Color Works	binds the green		51.54	20.70	excessive	3,512 pounds.
566	J. W. Metleer	Unknown	studding the green					
567	Kutner & Goldstein	Unknown	studding the green		48.78	12.70	excessive	60 pounds.
570	C. A. Duncan	Unknown	studding the green					
571	F. W. Braun & Co.	Eckstein Bros.	studding the green		53.84	9.80	small	
574	Langley & Michaels Co.	Atlantic Color Co.	some		52.47	4.93	small	1,220 pounds.

575	J. G. Thomas	Unknown		Many octahedrons				
577	E. E. Seely	Unknown	many	Few octahedrons				
578	Mrs. Ada McKelvry	Unknown	studding the green					
578	R. S. Hardie Baugh (Codlin Br'nd)	A. B. Ansbacher	studding the green					
582	Kirk, Geary & Co.	Adler Color Works	some	Few octahedrons	52.05	9.20	small	2,580 pounds.
586	C. H. Rodgers (Redington)		binds the green			16.90	excessive	
587	C. H. Rodgers (W. P. Fuller)		some			5.30	small	
588	C. Ford & Co. (Codlin Brand)	A. B. Ansbacher	many					
589	C. H. Rodgers (Codlin Brand)	A. B. Ansbacher	binds the green					
593	C. H. Rodgers (Ansbacher)		many			4.80		
594	Mack & Co.	A. B. Ansbacher	few and small		57.00	4.70	small	4,717 pounds.
595	W. P. Fuller & Co.	A. B. Ansbacher	few and small			5.50	small	
596	W. P. Fuller & Co.	Bulman, Warner & Co.	many			8.40	small	
613	J. W. Symmes	Unknown	many					
620	L. J. Harbison (Codlin Brand)	A. B. Ansbacher	many			5.10	large	
622	Maud Saunders		numerous	Many octahedrons		5.30	large	
631	J. F. Adams		many	Many octahedrons		5.40	large	
632	Carl Fredericks		very many	Some octahedrons		5.80	large	
640	S. C. Evans		many			6.40	large	

PHYSICAL AND CHEMICAL EXAMINATION.

There are no simple tests which will enable a person to quickly determine absolutely the purity of any given sample of paris green. A great many forms of adulterants, however, can be immediately detected. Samples showing any considerable variation in color, especially an abnormally pale shade, is an almost certain indication of adulteration, and those showing a tendency to dampness, or caking, should be rejected.

MICROSCOPIC EXAMINATION.

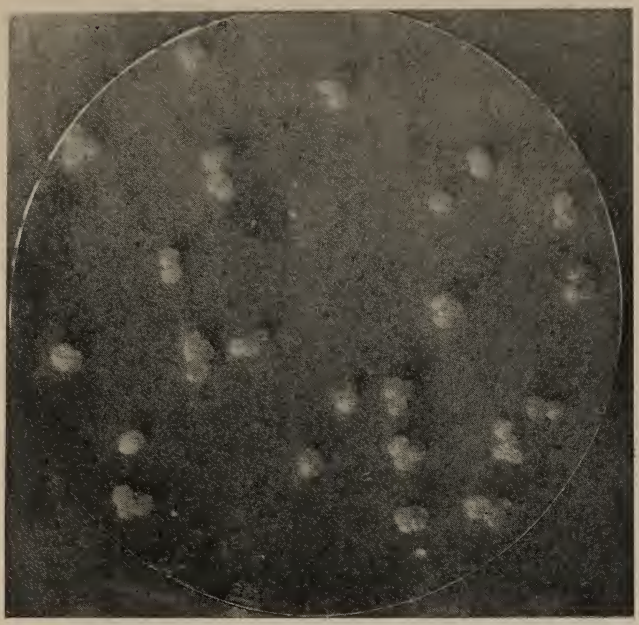
By far the most satisfactory of all the easy methods for the testing of paris green is the use of the microscope. For this purpose the sample is placed on a slip of glass, inclined and tapped gently so as to leave only a thin streak of green; the glass slip is then put under the microscope and examined with a medium-power objective, about one fifth inch. If the paris green is pure it may have several forms. If it is of old make, *i. e.*, five or six years old, manufactured by slow process, it appears as large, sharply defined *spheres* (Plate I), with only now and then a projecting crystal of "white arsenic"; if made recently by the rapid process, it appears in the form of *irregular*, sharp particles (Plate II, *a* and *b*), either large or small. Sometimes the particles are separate, sometimes adhering, but in both kinds the *projecting crystals* are few in number and not often large. There may also appear occasionally a loose *octahedron* of "white arsenic" mixed in what is called "broken-down" paris green. This latter is simply slivered material from the large globules, and is the result of over-crushing of the material when reducing it to a powder; if the focus of the microscope is changed a little, the real green color of these will appear.

In impure samples of paris green there will be observed, in addition to the above-described particles of either spherical or irregular shape, a considerable quantity of material of crystalline shape, usually of white color, the pure green being quite distinct from the adulterants as seen under the microscope, and as easily recognized as wheat can be distinguished from impurities that might be mixed with it. (Plate III.)

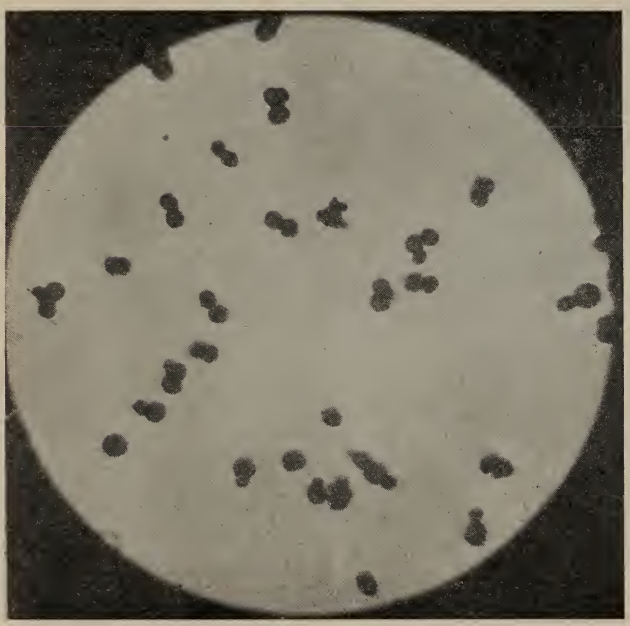
There is more difficulty in distinguishing paris green containing an excess of free "white arsenic." This sometimes is added in the form of a powder, and is then as easily recognized as any other form of adulterant; but when added or retained in the process of manufacture it is firmly attached to the particles of paris green, and only produces the effect of making them somewhat irregular, and causing a tendency toward sticking together (Plate IV); the grade of the material may vary greatly and can only be properly determined by chemical tests.

In the actual determination of "white arsenic" described in the following pages, the process consists simply of washing out the uncombined

arsenious oxid; Plate V, *a*, shows a sample as it appeared before washing, and Plate V, *b*, is the same after being washed only twenty-four hours.



By reflected light.



By transmitted light.

PLATE I. SPHERES OF PURE PARIS GREEN, OLD MAKE.

Inasmuch as some large New York manufacturers have sent out circulars for the purpose of trying to explain away the value of

the microscopic test of paris green, it is well to repeat our opinion of it. *The test furnishes conclusive evidence of the presence of "white*

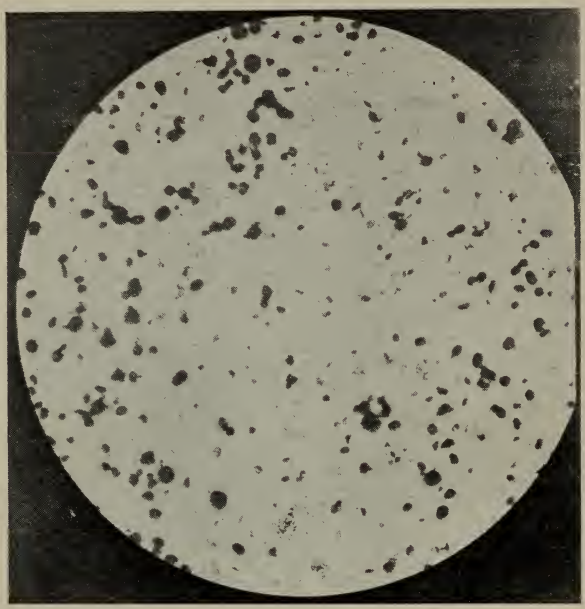


Fig. *b*. Fine.

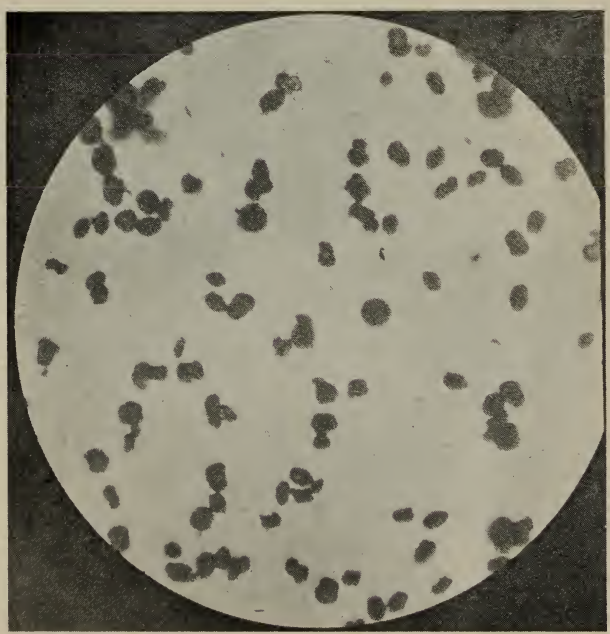


Fig. *a*. Coarse.

PLATE II. PURE PARIS GREEN, LATEST MAKE.

arsenic" in paris green; it seldom happens to-day that any green is so completely free from "white arsenic" in the form of characteristic

crystals that the latter can not be distinguished by this valuable and ever-ready test. These crystals are not to be confused with those of "broken-down" paris green produced by "scraping" and poor "bolting," as explained by the manufacturer. Because by these means the crystals are "whitened" or deprived of color, as in the case of grinding up copper sulfate, is no reason to expect or to imagine that they are ever converted into the shape of *octahedrons*, or remnants of these, or that they can be changed into anything which with careful observation can be mistaken for "white arsenic" crystals.

FREE ARSENIOUS OXID IN PARIS GREEN.

The amount of water-soluble arsenious oxid ("white arsenic") found in fifty samples of satisfactory paris green during 1900–1902 varies from 1.69 to 4.09 per cent, with an average of 2.84; in the other or objection-

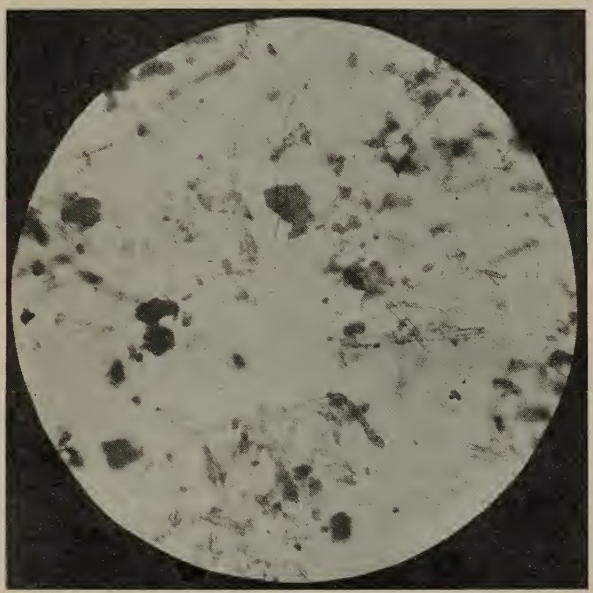


PLATE III. ADULTERATED PARIS GREEN.

able class, comprising fifty-four samples, this ingredient ranges from 4.70 to 29.40 per cent. At the New York Experiment Station (New York is the State in which paris green is manufactured) no objectionable ones have been reported and the content of "white arsenic" averaged for the year 1901 and 1902, respectively, 1.28 and 1.01 per cent in about the same number of samples that were examined here, and by practically the same method of analysis that we have adopted. Out of the forty-five samples examined during 1900 at the Bureau of Chemistry, Washington, D. C., it was found that according to the *four per cent standard* only thirteen specimens were passable, 71 per cent being found objection-

able. This is a worse state of affairs than was found by this Station, because the paris greens examined at the Washington Bureau of Chem-

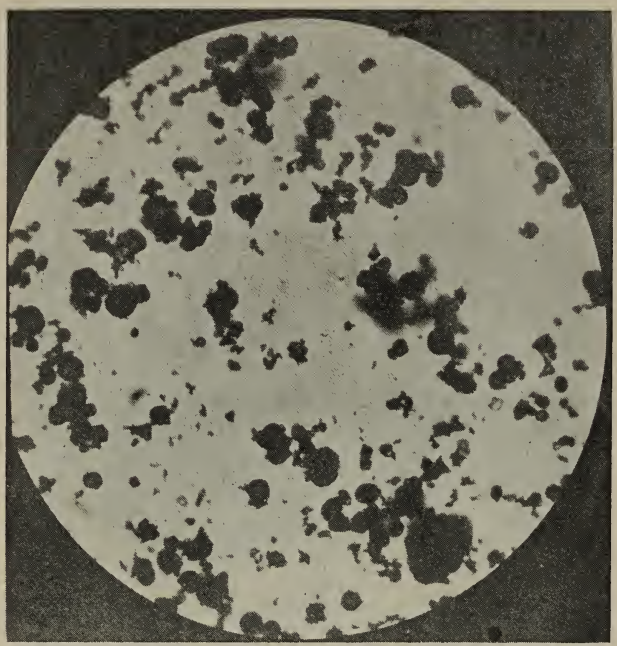


Fig. *b*.

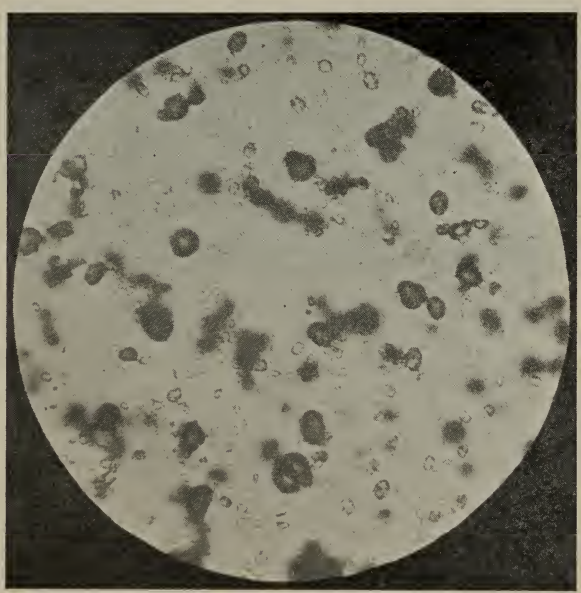


Fig. *a*.

PLATE IV. Impure Paris Green, Showing Loose and Projecting Crystals of White Arsenic.

istry were obtained from many Eastern States, by the Division of Entomology, U. S. Agricultural Department, Washington. It appears that

the farther away paris green gets from its place of manufacture (New York) the worse it is as to the content of "white arsenic," the leaf-

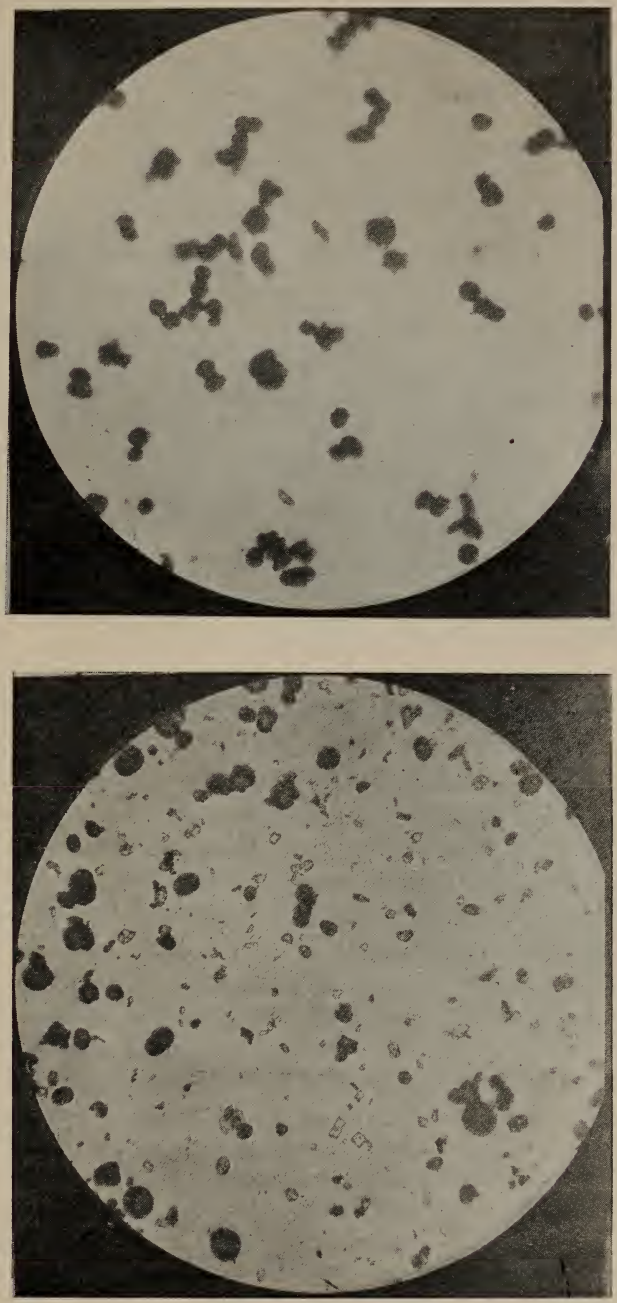


Fig. *a*. Before washing. Fig. *b*. After washing.

PLATE V. SAMPLE OF PARIS GREEN BEFORE AND AFTER WASHING OUT THE IMPURITIES.

destroying material. In other words, the orchardists of New York are furnished with a good class of the insecticide, while those of other States

have to put up with very much poorer grades, even when they have offered them the protection of a law governing its sale.

Aside from the injurious effects upon trees from the use of such paris greens as contain excessive quantities of "white arsenic," there is another aspect of the case, viz.: the *fraud* connected with the sale of such material. For, if from one tenth to one third of the weight of these materials is made up of *free* "white arsenic," worth only one third the price of good, passable, satisfactory paris green, it is not difficult to see that the manufacturers make large unearned gains upon ton lots. For example, if a wholesale dealer obtained $240 a ton for an article which contains one fourth free uncombined arsenious oxid, it is a simple matter to see that he has an unearned gain of about 17 per cent. By the time the *consumer*—the farmer—has his small lot of such objectionable paris green at 25 and 30 cents a pound, it becomes a very expensive material for his purpose, especially if he takes the trouble to add fresh lime to it, so that he has some surety that his trees will not be injured. He may as well take such well-known cheap material as london purple, which he knows must be mixed with lime to prevent injury to foliage, since it is sold to him as a waste product of the dye-works and is, therefore, of no very definite composition. One had better take the "simples" of arsenite of calcium or lead and make his own perfectly safe arsenical for the codling-moth, and thus save both money and trees.

METHOD OF DETERMINING WATER-SOLUBLE UNCOMBINED ARSENIOUS OXID OR "WHITE ARSENIC" IN PARIS GREEN.

As there has been some difference of opinion among chemists in regard to the solubility of arsenious oxid in water, we give below a concrete example of what we mean by washing the particles of paris green free from the projecting crystals of the oxid or "white arsenic" as compared with a treatment that has proven insufficient; and at the same time give the method as adopted by this Station.

A large lot of paris green had been condemned by this Station as containing more than 4 per cent of free arsenious oxid, though the consulting chemist of a New York firm of manufacturers had reported the presence of less than 3 per cent. This led to a comparison of methods upon the original condemned lot, and also an examination of the residue left after his treatment which was sent by the New York chemist as being free from the arsenious oxid.

Microscopic examination of the original sample: Projecting crystals of arsenious oxid mostly small; free octahedrons, few; "broken-down" paris green, considerable.

The *chemical examination* was made by two methods, viz.: by that described by a commercial chemist of New York City, and by the one used in the laboratory of this Station.

The method described by the commercial chemist may be called the "beaker" method. The temperature during this experiment varied from 20° to 23.5° C.

Beaker Method.—One gram of paris green, placed in 1 liter of distilled water for forty-eight hours at 20° to 23.5° C., with stirring every half hour during working hours (eight), yielded soluble arsenious oxid to the extent of 2.7 per cent, and the paris green residue, under microscope, still showed many remnants of projecting, lustrous crystals of arsenious oxid. One half gram of the dried paris green residue was thrown into the 500 cc. of first leaching, and allowed to digest for forty-eight hours more, with stirring as in first half of the experiment. This showed that more soluble arsenious oxid was present, to the extent of 2.25 per cent (of original substance used). A microscopic examination of this second paris green residue showed no projecting crystals or ridges of arsenious oxid, nor loose octahedrons of the same; apparently, too, the green had not suffered any change in texture or color. By this extension treatment, this sample, washed free from all adhering arsenic, is shown to contain a total of 4.95 per cent of soluble arsenious oxid. This is by no means so rigorous as that recommended by several Experiment Station chemists, wherein the time of treatment of one gram of paris green in 1,000 cc. of water lasts from *seven* to as many as *fourteen* days, at room temperature, for the complete extraction of soluble arsenic compounds, reported as arsenious oxid.

An examination of the New York chemist's residue, or *insoluble matter*, which he had obtained after treatment with water for forty-eight hours in his laboratory, was then made. This material under the microscope showed projecting crystals of arsenious oxid, and that many particles of paris green were impaired in color, *i. e.*, yellowish. One half gram of this working residue of paris green placed in 500 cc. of distilled water at a temperature of 20° to 24° for forty-eight hours, and stirred as above, showed by analysis that it contained 1.70 per cent of uncombined arsenious oxid, which added to the amount originally reported by him, 2.73 per cent, brings the total free arsenious oxid in the original green to 4.43 per cent. This *last* residue under the microscope showed no projecting crystals of *white arsenic*, and the particles of paris green had again assumed a green color.

Examination by this Station's Laboratory Method.—This takes into account not only the limits of orchard practice with paris green, but also reckons with the remarkable (?) properties ascribed to paris green by some chemists when it is treated with plain distilled water; regardless of the fact that this article—aceto-arsenite of copper—as manufactured to-day, is *instantaneously precipitated* from complex solutions containing alkali and often excessive quantities of various acids.

We, as customary, weighed half a gram of the sample of paris green into a 250 cc. Erlenmeyer flask and to it added 100 cc. of distilled water, *agitating, by shaking, every few minutes* throughout a working period (eight hours) of a day, keeping the liquid at only 25° to 30° C. The next day, after pouring off the clear liquid, a fresh 100 cc. of distilled water was added, and all this treatment was repeated on this and the following day—in all twenty-four hours. Finally the three 100 cc. leachings were combined, filtered through a double filter, and the water-soluble arsenious oxid determined. It amounted to 4.75 per cent of the original paris green. The residue from this experiment did not show under the microscope any lustrous crystals, either projecting or loose, of arsenious oxid—and the texture and color of the globules of green seemed unaltered.

The *three* results for *free arsenious oxid* in this paris green may be tabulated, for convenience, as follows :

	Per Cent.	
By method of New York chemist	2.73	4.95
Treatment of same continued by us	2.22	
Originally found by New York chemist	2.73	4.43
Found by us in the residue sent by him	1.70	
By method of this Station		4.75

We may, therefore, safely conclude that the "beaker" method of only forty-eight hours' exposure is insufficient for taking out all of the soluble "white arsenic," but an extension of the time to another forty-eight hours dissolves all this material from paris green. The copper dissolved in all of these tests only amounted to 0.10 per cent.

Many paris green samples from New York factories, when analyzed by this Station's laboratory method, fall into the "safe class," *i. e.*, those containing somewhat less than 4 per cent of free arsenic; and, to-day, we are reporting one with only 2.3 per cent. All of these tests have been controlled and confirmed by the microscope, which proved that all the water-soluble arsenious oxid was removed by washing.

The above simple form and description of the working of the method adopted by this Station was sent to the manufacturer's chemists in New York during the summer of 1901, and they obligated themselves to distribute it among the chemists interested in the manufacture of paris green, for the obvious reason that they all wished to be sure that the articles which they experted would in every case come within the law of California. Undoubtedly this method was well distributed, for since then there has been no correspondence on the subject with any manufacturing chemists.

Total Arsenious Oxid.—In fifty samples in which this determination has been made, only four yielded *less* than the amount required by law, *i. e.*, 50 per cent; and all of these greens with low total arsenious oxid appear in the class of objectionable ones (those classed as containing

excessive quantities of uncombined arsenious oxid). In no case where the green is otherwise satisfactory, is the total arsenic below the standard; rather, it closely approaches the theoretical amount in combination with copper in pure green, viz., 58.65 per cent, and often exceeds this figure. The significance of this outcome would be to establish the right to recommend the raising of the required amount of total arsenious oxid in green for horticultural purposes several points, and to be at least 55 or 57 per cent, by statute. The total arsenious oxid as taken by other Experiment Station chemists during the last year or two has apparently been raised by a point or two; and this, as observed by us in samples containing less than 4 per cent water-soluble "arsenious oxid." All of which means that manufacturers are approaching closely a *definite compound* of copper, "arsenic," and "vinegar"—a thing so much desired on all sides when they are improving the green in respect to water-soluble "white arsenic."

Copper, as Copper Oxid, in Paris Green.—A few determinations of this ingredient shows no great variation from 31.29 per cent as given for pure paris green; the results obtained here are quite similar to those obtained elsewhere, and all agree that ordinary green may contain from 26.5 to as much as 32.0 per cent of copper oxid. The *quantity* of *copper oxid* which goes into solution in the treatment of paris green with water is exceedingly small. In the course of twenty-four hours' treatment in determining water-soluble "white arsenic" the maximum amount found was only 0.30 per cent.

The value and use of these results belong to the future, since it is not possible with our present knowledge to make practical use of the water-soluble copper oxid determination.

ADULTERATION OF PARIS GREEN.

This Station has never yet analyzed a sample of paris green in which adulterants were added to the extent reported of foreign paint materials. This is also the experience of several Eastern experiment stations. In Germany the case is quite different, for much adulterated green is found containing barium sulfate, calcium carbonate, chrome yellow, iron oxid, lead chromate, etc. In part these materials are simple make-weights, while others are added in order to produce different desired tints of color.

Such materials as barium sulfate, fine sand, calcium carbonate, etc., are easily recognized by their insolubility in ammonia, and so we have a very easy way of detecting them in paris green, which completely dissolves in this liquid, turning it to an intense blue color.

This test, however, is not conclusive, since white arsenic and a number of other substances used in adulterating paris green, especially in these later years, are soluble in ammonia and would escape detection if this

method alone were depended on. Insolubility of any portion of it in ammonia, then, affords valid grounds for rejecting a sample; but other means must be used to be sure of its purity, even if apparently pure by this test.

This is still more emphasized when it was found that many commercial chemists last year made a common mistake in regard to their interpretation of the result of the ammonia test with paris green, viz.: in concluding that because the material is completely soluble in ammonia "therefore it is free from white arsenic." Now, "white arsenic" is itself soluble, and at this Station we have repeatedly mixed various grades of it with paris green, even up to equal proportions of these materials, and treated them with cold ammonia in the proportion of one to ten, and have yet to find a case in which all the "white arsenic" failed to dissolve; and this is accomplished in a few minutes, instead of taking hours as announced by some. The reason for this error by commercial chemists is not far to seek, when a prominent Eastern experiment station chemist in a bulletin states most clearly that "the insolubility of paris green in strong ammonia is a fair test of purity, so far as concerns the addition of white arsenic and insoluble adulterants like calcium sulfate, barium sulfate, etc. We have indicated those samples that dissolve easily and completely in strong ammonia, making a perfectly clear solution without sediment. These samples were free from "white arsenic."

One has only to consult a few authorities to find that "white arsenic" is classed as soluble in ammonia; for instance, Storer's Dictionary of Solubilities, under "Arsenious Oxid," says, "Readily soluble in aqueous solution of arsenite of ammonia (or in caustic ammonia)," etc. Comey's Dictionary of Chemical Solubilities, p. 30, Arsenious Oxid—"Easily soluble in alkali hydrates, or carbonates plus water." U. S. Dispensatory, 17th edition, p. 24, makes note of solution of arsenious oxid in ammonia as tests for impurities in the white arsenic. Wormley's Micro-chemistry of Poisons, at page 256, reads, "Arsenious oxid is readily soluble in solutions of the fixed caustic alkalies, but is much less soluble in ammonia." Douglass & Prescott's Qual. Chem. Anal., p. 112, "Arsenious anhydride is readily soluble in alkali hydrates with combination." Graham-Otto, Lehrbuch der Chemie, Vol. 3, p. 472: "Kalilauge, Natronlauge und Ammoniakflüssigkeit lösen die arsenige Säure in reichlicher Menge auf, ohne dass die alkalische Reaction verschwindet, damit Arsenigsäure-Salze bildend (siehe diese unten). Die Auflösung in Ammoniakflüssigkeit hinerlässt bein Verdampfen arsenige Saure (siehe oben; ferner unten: arsenigsaures Ammon.)."

It may generally be said of paris green in this market, so far as the samples examined here represent the condition, that there is hardly ever any practice of adding "make-weights," such as marble dust,

gypsum, etc. This has also been the experience of the secretary of the State Board of Horticulture of California.

This market is fast coming to be in very fair condition as to samples which come within the law, and especially those containing *less* than 4 per cent of "white arsenic"; still there is much room for improvement as compared with the reported condition in this respect of the paris greens on sale in New York State, where *all* are satisfactory, according to the findings of the Agricultural Experiment Station at Geneva, New York.

CHARACTER AND VALUE OF SOME OF THE LATEST COMMERCIAL SUBSTITUTES FOR PARIS GREEN.

The extensive use of london purple as a cheaper arsenical insecticide than paris green, and the widespread recommendation of all the entomologists of this country to *mix it and paris green with an equal weight of fresh lime* for the neutralization of the uncombined arsenic in it, have given the manufacturers of arsenical insecticides an excuse for making and offering for sale many patented compounds of arsenic, lime, and copper; of course the many failures from the use of poor paris green also help them out. Some are imitations of paris green; often they contain little, if any, green-colored arsenite of copper, and even lead arsenite has been dyed green and sold as "Green Arsenite." Now london purple, Scheele's green or "green arsenite," and lead arsenite, are, when properly compounded, safe insecticides, and equal to paris green in value against insects. What we wish to show is that the majority of the later and cheap commercial combinations of *lime*, *arsenic*, and *copper* are poor substitutes for satisfactory paris green, and that they hardly ever possess the chief property of *not containing leaf-scorching materials*, as is universally claimed for them. Also, that they are *heavier materials* than would appear from the ordinary commercial description of them.

Among these arsenicals the following have been examined at this Station: Paragrene, Laurel Green, Calco-Green, and the various green, white, red, and gray Arsenoids.

Paragrene.—A recent arsenical spraying material is a patented article bearing the name "Paragrene," samples of which have been received for examination by this Station. The manufacturers of paragrene claim "that the article was very extensively used last year by planters and growers all over the country, and that it is free from the objectionable features of paris green, in that it does not burn or scorch the most tender foliage. It contains the required percentage of arsenic as arsenious oxid. Besides this, the article is considerably cheaper than paris green." It retails at from 13 to 17 as against 25 or 30 cents per pound for paris green.

A microscopic examination shows that this material contains, besides

the ordinary green, a considerable quantity of sulfate of calcium (gypsum) and also many crystals of "white arsenic."

The substance analyzed as follows:

	Per Cent.
Copper oxid (CuO)	23.46
Arsenious oxid (As_2O_3), combined	17.52
Arsenious oxid (As_2O_3), free	23.08
Acetic acid	6.72
Calcium sulfate (gypsum)	19.31
Sodium sulfate	2.26
Sodium chlorid	.25
Peroxid of iron	.20
Water	6.20
Total	99.00

Notwithstanding that the above composition complies in many particulars with the claim made for it in the Patent Office, the fact that it contains so much (nearly one fourth its weight) of *free, water-soluble arsenious oxid* stands against it. In this sample of paragrene the free arsenious oxid is as high as in some of the most objectionable paris greens. This article, therefore, must be rejected, as it will positively cause injury to foliage if used in California orchards.

Laurel Green.—Manufactured by the Nichols Chemical Company, New York. Composition:

	Per Cent.
Gypsum (land plaster)	50.0
Calcareous sand (greensand)	20.2
Arsenite of copper	24.7
Moisture, etc.	5.1
Total	100.0
Soluble arsenic compounds	.8

All such articles as this analysis shows this laurel green to be can never be recommended for spraying purposes, because they do not contain enough arsenic to make them effective when used according to the usual formulas. This material consists chiefly (three fourths) of gypsum and greensand, both of which are only in the way in spraying operations. The greensand shows a very poor attempt at plain fraud. No matter how cheap this article is it will not pay to handle it for fighting insects.

Calco-Green.—This is offered as a cheap substitute for paris green, the price being 9 cents a pound. It is a gray-green fine powder containing:

	Per Cent.
Total arsenious oxid	30.0
Water-soluble arsenious oxid	7.0

This, besides being an unsafe material because of its large content of soluble arsenic, has too little total arsenic to make it worthy of trial even in an experimental way.

Gray Arsenoid (Calcium and Copper Arsenite) is thus described by the maker who sent a sample to us for examination: "This arsenite of copper and lime is so prepared that it is absolutely free from *uncombined arsenious oxid* and has an alkaline reaction. While the percentage of total arsenious oxid (guaranteed to be 38.30) is not as great as that of paris green, it has the advantage that it can be used in any strength as a spray without injury to the foliage. Being a comparatively inexpensive article (8 cents per pound), a greater strength of solution can be used at the same cost, thus overcoming the differences in the efficiency that exist in solutions of equal strength. It has the advantage of a comparatively very small specific gravity, which prevents it from settling speedily in water; thus forming a spray of uniform strength, which in the case of paris green involves considerable difficulty."

Analysis of Gray Arsenoid.

		Per Cent.
Moisture		16.10
Arsenious oxid (combined)	21.24	35.00
Arsenious oxid (uncombined), soluble	13.76	
Copper oxid		15.10
Calcium oxid		27.10
Carbonic acid, Prussian blue, sodium sulfate, etc.		6.70
Total		100.00

The result of the examination of this arsenoid leads to an unfavorable conclusion, and chiefly on account of the *soluble* arsenic in it, which amounts to 13.74 per cent. It appears that this material (aside from its copper and absence of dye) resembles london purple, but may be rated superior to it because it shows considerably less soluble arsenic. This arsenoid, like the familiar article named above, when used, perhaps may have the soluble arsenic in it corrected or neutralized by mixing it with an equal weight of fresh lime.

White Arsenoid (Barium Arsenite).—This material upon analysis was found to be of the following composition :

	Per Cent.
Barium carbonate	44.05
Barium chlorid	13.05
Barium oxid	8.18
Arsenious oxid, free	27.64
Lead carbonate	1.86
Silica	.20
Moisture	4.00
Total	98.98

The only ingredient which might give this compound a value for spraying trees is the arsenious oxid. But all of this oxid is in such a condition that it is extremely dangerous to foliage, and practical tests have shown it to be so. Probably the other soluble barium compounds act

as poisons upon plants. Of the other components, the largest, barium carbonate, simply makes weight and adds nothing to its value. The same is true of all the other ingredients. Notwithstanding that this material is offered for a much lower price than paris green, it can not be safely recommended.

Green Arsenoid (Copper Arsenite).—This compound is "dead" green in color, and under the microscope is seen to be a mass of irregular, sharp crystals. It shows the presence of some *soluble blue*,* which often contains arsenic. It analyzes as follows:

		Per Cent.
Copper oxid (CuO)		28.83
Arsenious oxid (As_2O_3), combined	53.51	61.33
Arsenious oxid (As_2O_3), free	7.82	
Moisture		2.77
Silica		.40
Organic matter derived from *soluble blue*; sulfate of soda, etc.		6.67
Total		100.00

While this material contains the guaranteed quantity of arsenious oxid, and is cheaper than the common green, still it is hardly safe, as it stands, to use in this climate, with its nearly 8 per cent of free arsenious oxid.

Pink Arsenoid (Lead Arsenite).—This material is colored with some pink-colored aniline residue, and shows the following composition by analysis:

	Per Cent.
Lead oxid (PbO)	49.58
Arsenious oxid (As_2O_3), combined	40.02
Arsenious oxid (As_2O_3), free	3.24
Moisture	.31
Organic matter from aniline residue; lead sulfate, etc.	6.85
Total	100.00

This compound can not be objected to, and a practical test with it shows that it is perhaps but little, if any, more dangerous to foliage than paris green. It is sold for much less than ordinary green; this, when considered with the low content of free arsenious oxid, should recommend it.

Conclusions Regarding These Commercial Substitutes.—It appears from the foregoing record that of these "arsenoids" the lead compound is the best; *i.e.*, the least injurious. The copper compound is certainly promising, and if proper methods are followed in its manufacture it can easily be made a desirable insecticide. But of the barium compound nothing more need be said than that it is simply worthless. It is a grave mistake to put it on any market for the use for which it was intended.

*Sodium triphenylrosaniline-monosulphonate.

The *physical properties* of these commercial substitutes, especially those which determine and show how long they will remain in suspension in water, have been studied and the results are given on page 34.

It will be seen there that all but one of them, the pink arsenoid, show no more advantage in this respect than london purple does over finest powdered paris green. Briefly, they remain in suspension only *twice* as long as paris green, which, to say the least, means that they are not high-grade materials, and therefore they are disappointing from this point of view. But of all the cheaper compounds of later make offered to take the place of the expensive paris green, only one, the *pink arsenoid*, can be with safety recommended to the orchardist as not liable to burn his trees.

The conclusion that these articles do not answer the purpose for which they were intended is quite in accordance with the generally accepted one regarding all proprietary articles, no matter of what description, offered as insecticides or fungicides, viz.: that they seldom are what they are claimed to be, and often are of little or no value against pests, or even as fertilizers if they should happen to fall upon the soil.

In view of these facts the orchardist should consult some authority before purchasing any article of this kind, in order that its composition and qualities may become known to him. This he should first do by inquiry of his own Agricultural Experiment Station, in order not only to save his cash in hand, but also to increase the yield of his orchard by avoiding the burning of the leaves of the trees upon which he is advised by some dealer to put such poor materials.

HOME-MADE ARSENICALS.

(These comprise compounds of lead and arsenic, and of lime and arsenic.)

There seems to be no good reason why these may not be used in all places in spraying where arsenicals are employed, for they possess the following excellent properties, viz.: *first*, they are easily made, and the resulting compounds from the "simples" have the most definite composition among the arsenicals used; *second*, it can be shown that they are the cheapest arsenicals; *third*, that the lead arsenicals are the most insoluble of all combinations of arsenic and metals, and therefore the least liable to burn the foliage, no matter how delicate it may be; *fourth*, these materials do not, like paris green, require a constantly-working agitating machine in the process of spraying—a turn of the machine now and then will be enough to keep them in suspension, and therefore insure an even distribution of the poison over the whole orchard; *fifth*, practical tests with them show that their action is excellent from all points of view.

LEAD COMPOUNDS.

Arsenate of Lead.—There are two methods of making this compound—either by mixing the ordinary acetate of lead (*sugar of lead*), or the more expensive nitrate of lead with the best quality of arsenate of soda. The resulting compounds are of slightly different composition, but of equal effectiveness against insects in their poisoning properties.

Since it is an important matter to know the composition of the ingredients used in the manufacture of arsenate and arsenite of lead, we give the following information for the guidance of the purchaser: The articles to be used are acetate of lead (sugar of lead) and arsenate of soda. They should be guaranteed to be first class, and, if necessary, the purchaser may have their composition determined at the Experiment Station.

First-class crystallized lead acetate (sugar of lead) should contain about 58.8 per cent of available lead oxid, but it dries out or loses some water in the air and thus ordinarily contains from 60 to 62 per cent. It is readily soluble in cold water in the proportion of one pound to one gallon of water. In hot water it readily dissolves in a less quantity, and for its quick solution hot water is always preferable. This is the cheapest water-soluble lead salt in commerce, and therefore will probably be used most frequently. Its wholesale price is $7\frac{1}{4}$ cents per pound.

Arsenate of soda should have not more than 2 or 3 per cent of chlorin, as this changes the lead acetate into lead chlorid, thus occasioning waste; lead chlorid being of no value as an insecticide. What is known as "sixty-eight per cent" arsenate of soda contains about 47.8 per cent of arsenic acid and only 0.57 per cent of chlorin. The remainder of the material consists of the normal materials entering into its composition; *i. e.*, soda, potash, water of crystallization, a trifling amount of sulfate of soda, and insoluble matter. This salt is very soluble in hot water, which is preferable for its solution. The wholesale price of arsenate of soda is 5 cents per pound.

The formula for making one pound of lead arsenate, *i. e.*, enough for from 100 to 150 gallons of water, is to dissolve 24 ounces of acetate of lead (or 20 ounces of lead nitrate) in one gallon of cold water; also separately 10 ounces of arsenate of soda in three quarts of water; both in wooden vessels. These weighed quantities can be bought in separate parcels and are superior to any mixture of them which may be offered. The separate solutions are to be poured together into the spray tank filled with water. A white precipitate of lead arsenate ready for spraying immediately forms in the tank; its fine flocculent condition keeps it in suspension for hours, and of all arsenicals it is the most easily kept suspended in water.

The above is the ordinary recommendation; but the preparation can be used several times stronger if desired, without the least danger of producing any injury to foliage, even if used at the rate of from 3 to 15 pounds to 100 gallons of water.

To prove conclusively that this spray liquid contains lead in excess, as it should, one has only to take out a little of it and test it with a few drops of potassium bichromate, when there should be a yellow-colored precipitate.

Lead arsenate, made as above directed from the best quality of both lead acetate and soda arsenate, has the following composition:

	Per Cent.
Water	2.37
Lead oxid (PbO)	73.10
Arsenic pentoxid (As_2O_5)	21.80
Chlorin	2.40
Total	99.67

In the market there are now found several kinds of lead arsenate ready for use; sometimes it is a dry powder, white or colored with a dye, and sometimes a paste mixed with tar or glucose to make it stick to foliage or to attract insects. Such a compound as the latter is "Swift's arsenate of lead." A sample of the white dry powder variety was shown by analysis here to contain 25.90 per cent of arsenic pentoxid, 68.06 per cent of lead oxid, and 1.16 per cent of chlorin, the rest being principally water. There were present 0.80 per cent of water-soluble arsenic compounds.

Swift's arsenate of lead, in the form of paste, usually has the following composition, as shown by an analysis recently made in this laboratory:

	Per Cent.
Lead oxid	36 00
Arsenic pentoxid	12.00
Organic matter (glucose) and other organic matter	9.00
Water	43.00
Total	100.00
Water-soluble arsenic oxid	0.15

While both of these have the requisite amount of actual poison to make them, in practice, sufficiently strong when made up with the usual quantity of water, they do not come up to the standard when compared with *freshly* precipitated, home-made lead arsenate, for they settle in the spray tank much quicker. Of course the dry form settles quickest, but remains in suspension about four times as long as the finest-powdered paris green; while the home-made lead arsenate will remain suspended *fourteen times* as long.

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"*Disparene*" is the trade name for a much-advertised new form of arsenate of lead, a bluish-gray colored *paste*, which the makers—The

Bowker Insecticide Company of New York—describe as "a most concentrated form of arsenical poison, put up in the shape of a dense, heavy white paste, which mixes well with water, although it is not soluble. Its complete insolubility makes it perfectly safe to apply at any desired strength without burning or scorching the foliage. In this and in its great adhesive qualities, lies its superiority to paris green and all other arsenical insecticides."

"Disparene is used with water at the rate of two or more pounds to fifty gallons, and retails for 25 cents a pound."

A sample of this grayish-blue paste has just been received here, and by analysis has the following composition:

	Per Cent.
Water and volatile oil	30.5
Lead oxid (PbO)	49.0
Arsenic pentoxid (As_2O_5)	16.3
Tar and other organic matter	4.2
Total	100.0
Water-soluble arsenic oxid	0.3

This material, as is claimed, is thus shown to be a somewhat stronger poison than Swift's, and like it and the Adler lead compounds contains very little water-soluble arsenic compounds. On the average for these three, this matter amounts to only one tenth as much as is allowable in paris green. These articles, therefore, are perfect compounds as to freedom from leaf-burning ingredients. But disparene, unlike what is said of it by its manufacturers, will always have this against it, viz.: that it is difficult to break up this tenacious paste and mix it with water without leaving heavy lumps in the bottom of the spray mixture. Swift's lead poison, on the other hand, is easy to work up in water.

For the same money that one spends on such goods a farmer can have either arsenate or arsenite of lead spray of his own make which contains as much poison, and, moreover, will remain in suspension in water nearly half again as long a time.

Arsenite of Lead is prepared by dissolving separately 12 ounces of sodium arsenite (retailing at 10 cents per pound) and 4 pounds of lead acetate in water, then pouring them into a 150-gallon spray tank filled with water, when there is obtained a milky mixture ready for spraying operations. Such a perfect mixture of di- and tri-plumbic arsenite will remain in suspension nearly *fifteen times* as long as the finest-grained paris green. Another quality that makes it of special value is that it can, like lead arsenate, be applied many times stronger than recommended above without any danger of scorching leaves. The home-made arsenite of lead remains in suspension four times as long as does its commercial relative, the "pink arsenoid," mentioned above.

Lime Compounds of Arsenic.

Several formulas are given for making these sprays, and all yield the same form of poison, viz.: *calcium arsenite* (tri-calcic arsenite), about the insolubility of which in water, when made in the spray tank and used immediately, there is no dispute. However, if these compounds remain in contact for long periods of time (days and weeks, not hours) in water they suffer a little decomposition, whereby soluble arsenites are formed; and it is certain that foliage can not stand more of these than it can of free "white arsenic." The several formulas for making this arsenite (such as Taft's, Kedzie's, and Smith's, although these persons did not invent them) are known, and are given in California Bulletin No. 123, the supply of which is unfortunately nearly exhausted.

"*Arsenic and Lime*" (Taft's Formula).—Very satisfactory directions for making this mixture are given in a letter from Professor Taft, of Michigan, one of the first who extensively experimented with it; he writes: "I have had excellent results from boiling one pound of [white] arsenic and two pounds of lime in two gallons of water for forty minutes and then diluting as required. When one pound of the arsenic prepared as above, is used in every three hundred to four hundred gallons of water, I have found it equal to paris green for destroying codling-moth and curculio, while one pound answers for one hundred and fifty to two hundred gallons of water when it is used upon potatoes; unless used in Bordeaux mixture, I find it best to add a small amount of lime when diluting. As the wholesale price of arsenic has averaged about seven cents per pound for a number of years, while paris green has wholesaled at eighteen cents, it is evident that the latter is fully five times as expensive." In reference to the comparative value of arsenic used with soda and lime, he further writes: "While some recommend the use of sal soda to dissolve the arsenic, we have not found it necessary; and as the use of soda at the rate commonly recommended nearly doubles the expense of the spraying mixture, we have not recommended it, although the claim that when sal soda is used it is possible to tell when the arsenic is dissolved, is correct." The only trouble with this mixture seems to be the danger of an incomplete union between the lime and the arsenic, so that the full forty minutes' boiling, even with more lime and the addition of lime when diluting, would probably render the mixture entirely safe.

"*Arsenic, Soda, and Lime.*"—This is often known as the Kedzie formula. The combination of these three materials yields insoluble tri-calcic arsenite—the arsenious oxid in the sodium arsenite (formed by dissolving "white arsenic" in common sal soda) uniting with the calcium of the oxid of calcium, or lime. The reason for entering so explicitly

into the description of the action of the components of this formula is that some have tried to make it with only two of the ingredients, "white arsenic" and soda; in their haste they leave out the vital elements of the formula, the fresh lime. Of course their trees were spoiled, as only arsenate of soda was formed, which burns the leaves immediately.

The method of production is fully described in the following letter under date of September, 1899, from the late Professor Kedzie, of the Michigan Agricultural College:

> The formula I recommended for an arsenical spraying mixture to take the place of paris green was the following: Boil two pounds of white arsenic with eight pounds of sal soda in two gallons of rain water. Boil these materials together in any iron pot not used for other purposes; boil them fifteen minutes, or until the arsenic dissolves, leaving only a small muddy sediment. Put the solution in a two-gallon jug and label *Poison, Stock material for spraying mixture.* The spraying mixture can be prepared whenever required in the quantity needed at the time, by slaking two pounds of lime, and adding this to forty gallons of water; pour into this a pint of the stock arsenic solution; mix up, stirring thoroughly, and the spraying mixture is ready for use. The arsenic in this mixture is equivalent to four ounces of paris green.
>
> ADVANTAGES OF THIS METHOD: *First*—It is very cheap and the materials can be found in every village in the State;
>
> *Second*—The stock material (arsenite of soda) is easily prepared and can be kept in that form for any length of time, ready for making a spraying mixture of lime and water;
>
> *Third*—The arsenite of lime in the quantity required for spraying will not burn the leaves or injure the trees or plants;
>
> *Fourth*—It will be uniform in quality and not vary in strength, as paris green often does;
>
> *Fifth*—It makes a milk-colored spray and the color on the trees will show how evenly it is distributed.
>
> Every one using such deadly poison should bear in mind the possible danger from its use; the pot, the jug, and every apparatus for making the arsenite of soda should be used for no other purpose of any kind.

Mr. Smith, of Hood River, Oregon, varies this formula, recommending: "Instead of two pounds of lime I used not less than six pounds; and I found that the additional lime prevented burning foliage and also retained the poison longer on the trees. I also used one quart instead of one and a half pints of the arsenic to fifty gallons of water." And again, "I would recommend using freely of the lime up to say ten pounds to fifty gallons of water."

Arsenite of calcium has been found by us to remain in suspension longer than finely powdered paris green and somewhat longer than its commercial relative, london purple, which, when used with fresh lime, probably becomes tri-calcic arsenite, the dye part of it having no value as an insecticide. Arsenite of calcium, and even paris green made up with lime, has, when sprayed upon fruit (apples, for instance) nearly ready for the market, given the fruit a "whitewashed" appearance; this is the only complaint about it on this side of the subject which has reached us. But this is easy for the farmer to avoid.

DANGER FROM THE USE OF ARSENICAL MIXTURES.

It should be borne in mind that arsenic is a very dangerous poison and that in any form it may be fatal to man or animals; especially should care be taken in the manufacture of the home-made compounds, as the handling necessary in these cases increases the danger from poisoning through carelessness. Properly handled, arsenic is perfectly harmless, and there is no excuse for any one becoming in any way affected by it. There is in the minds of a few people some apprehension that bad results might follow from the use of fruit protected by spraying; but this apprehension is certainly without foundation. There is yet to be the first case of injury resulting in this way. In all reported cases that have come under our observation the symptoms were in no case anything like those that might be produced by the arsenic. It is, nevertheless, true that a certain amount of arsenic remains on the fruit, and that no one sprays any considerable time with the arsenites without getting some of the material into the mouth or lungs; in some cases even enough to be recognized in the excretions. We have known a few cases in which the person applying the poison was careless enough to become very slightly affected, the symptoms being those of chronic arsenic poisoning. These cases simply show the need of great care in handling the poisons, though this can be done with perfect safety when care is taken.

SOME PHYSICAL PROPERTIES OF ARSENICALS.

All experimenters with arsenicals agree with the facts contained in the following statements, and emphasize them in their writings.

One of the most important points in every insecticide applied with water is the *time it will remain in suspension.* If the arsenite sinks to the bottom of the spray tank in a few minutes, as does paris green, there is always an unequal distribution of the poison, and the concentrated mixture at the bottom is almost always sure to "scorch" foliage. Generally speaking, the lighter and more flocculent an arsenite is, the longer it will remain in suspension in the tank. So those arsenites of high specific gravity, especially the *dry* powders, like paris green, Scheele's green, paragrene, and dry lead preparations whose gravities are all upward of 3.1 (*i. e.*, higher than that of quartz sand with 2.6 specific gravity), are objectionable, because continuous stirring is required to keep them in suspension. This will always stand against paris green, no matter how pure, or how valuable an insecticide it may be.

In order to bring out some of the facts relating to the power of different arsenicals to remain in suspension, we have made a series of tests with the different spray mixtures, using the same amount of each poison in each experiment, all at the rate of 1 pound to 150 gallons of water. The following diagram shows the time, in minutes (the numerals after each shaded column), that is required for the settling of each arsenical

through a one-foot column of the water of the practical spray mixture. The shaded columns show at a glance the variations.

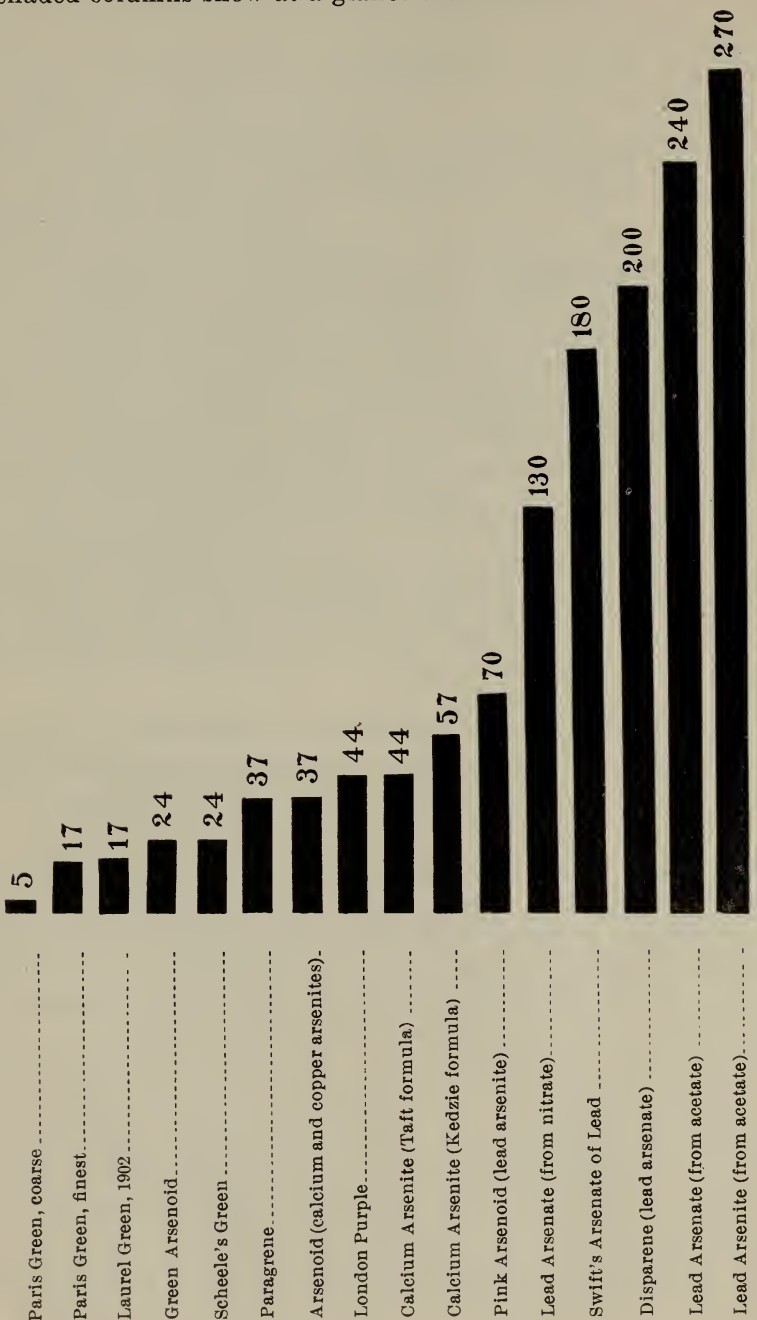

PLATE VI. Diagram Showing Time in Minutes Required by Various Arsenicals to Settle Through 12-inch Column.

Here it is readily seen that the arsenites and arsenates of lead easily lead all other materials in remaining in suspension; and those of this group that are capable of home-made production show the greater

superiority. As before stated, the *arsenite of lead* made by pouring solutions of lead acetate and sodium arsenite in the filled tank rates the highest; next comes the *arsenate of lead*, and both may be roughly stated as remaining in suspension some fourteen or fifteen times longer than the highest grade of finest powdered paris green, and over fifty times as long as the coarse-grained green.

The arsenate of lead compounded with glucose (Swift's) makes a fair showing when compared with the home-made product, in the proportion of 10 to 14 (fine paris green being the standard in all cases), rating even higher than the arsenate of lead made from *lead nitrate*, which is found to remain suspended only eight times longer than fine paris green.

When we leave the home-made poison with lead base there is seen to be an immediate and extraordinary falling off in the power of all other arsenicals to remain in suspension; the arsenite of lime (Kedzie formula) being only three times better than fine paris green.

It is interesting again to see here how well some manufacturers of arsenical insecticides turn things to their pecuniary advantage; witness how easily the farmer is to be imposed upon in the advice long ago given by careful experimenters "to *color* any white powder around his place containing arsenic, in order that it may not be mistaken for a harmless white one";—the *pink arsenoid*, green arsenoid, etc., all give in water the various colors which their names carry; and these colors in the liquid give the impression that the poison remains long in suspension, when in reality by tests it has been shown that the arsenic is at the bottom of the tank. The various dyes, then, mask the speedy settling of the poison, and have been added for that purpose. In none of these artful preparations is this property of staying up in water developed to any particular extent; in any event, it may be safely put at only about twice as high as that of first-class paris green.

COST OF ARSENICALS.

It is customary among writers on this important point to give statements showing simply the retail price of different poisons to the farmer; sometimes the wholesale price is given. Besides these, two others, very infrequently met with, can safely be furnished, viz.: the cost of the arsenical in the various formulas, and also the cost of these when upon the tree.

Briefly, from the first point of view the common arsenicals stand in the following descending order in prices per pound: paris green, disparene, paragrene, Swift's arsenate of lead, Scheele's green, green arsenoid, london purple, and, the cheapest of all, the arsenites of lime. The rarer arsenate and arsenite of lead are the most expensive arsenicals used for fighting insect pests, but they are said to be applicable at almost any strength without any danger of burning foliage.

From the second standpoint, viz., the cost of the arsenicals as furnished by the different formulas for making and applying them with water, the table below is given to show how they stand:

COST OF DIFFERENT ARSENICAL SPRAYING MATERIALS.

	Lime, @ 1 cent.	Arsenious Oxid or White Arsenic, @ 7 cents.	Sal Soda, @ 3 cents.	Total Cost per lb.	Gallons. In Formula	Gallons. For One Dollar	Relative Strength of Arsenic in 100 Gallons.
							Ounces.
PARIS GREEN	------	------	------	$0.20	150	750	5⅓
ARSENITE OF LIME—							
Kedzie formula	$0.32	$0.14	$0.24	.70	640	914	5
Smith formula	.80	.14	.24	1.18	400	339	8
Taft formula	.22	.07	------	.29	400	1,379	4
	Arsenate and Arsenite of Soda, @ 10 cents.	Lead Acetate, or Sugar of Lead, @ 14 cents.	Lead Nitrate, @ 16 cents.				
ARSENATE OF LEAD—							
From sugar of lead	$0.06	$0.21	------	.27	150	555	3⅓
From lead nitrate	.06	------	$0.20	.26	150	577	3⅓
ARSENITE OF LEAD—							
From sugar of lead	.075	.63	------	.71	150	212	5

Here it appears that more gallons per dollar can be had by the arsenite of lime (Taft formula) than by any other, although the arsenic in it per gallon is lower than that in paris green, or only 4 to 5½ ounces per 100 gallons; but all are claimed to give equal satisfaction as far as killing the codling-moth is concerned. One dollar buys, as we see, only one fourth as many gallons of lead arsenite as it does of paris green spray.

When the arsenical is finally upon the tree—the last place to consider its cost—it may easily be seen from the little table below that after all that may be said about the original cost of arsenicals and the cost of preparing the spraying liquid, they amount to practically nothing when the labor of application to the tree is considered. For the cost of one treatment for a tree of average size (one gallon per tree) with the different arsenicals named, including the cost of preparation of mixtures and labor employed in applying them, is perhaps not far from the following:

COST OF ONE TREATMENT WITH DIFFERENT KINDS OF ARSENICALS.

	Total Cost per Tree.
Paris green and lime	$0.0563
London purple and lime	.0555
Arsenates of lime—	
Kedzie's	.0567
Swift's	.0585
Taft's	.0562
Arsenate of lead, from sugar of lead	.0568
Arsenite of lead, from sugar of lead	.0666

All of which simply means that if one can himself make safe materials for fighting the insects which destroy his crop, he has the remedies not only against them but against the use of impure, costly materials which are frequently offered by the trade.

SUMMARY.

The results of the examination of paris green and other arsenical spraying materials may be summarized as follows:

First—That this market is fast growing to be in very fair condition as to the *quality* of the paris green found in it; more and more of this poison coming within the requirements of the law, especially as regards those containing less than *four per cent* of "white arsenic." Still there is much room for improvement as compared with the paris green on sale in New York State, where, according to the reports of that Experiment Station, *all* are satisfactory.

Second—That adulteration in the sense of adding foreign matter, "make-weights," to paris green (*marble dust*, *gypsum*, *barium carbonate*, etc.) is rarely practiced in this country, at least by the manufacturers.

Third—That the examination of paris green, both as regards the physical and chemical tests, is not as an obscure a matter as was formerly claimed by some chemists.

Fourth—Few of the commercial substitutes are found to be passable as regards the water-soluble arsenic compounds in them; and for this reason and because they possess little advantage over paris green in remaining in suspension in water, they are not to be taken up indiscriminately by the farmer upon the word of the trade.

Fifth—That the insoluble arsenate and arsenite of lead and arsenite of calcium (home-made arsenicals) are to be recommended for extensive trial, especially the lead compounds, when heavy doses of poison are required.

An Act to prevent fraud in the sale of paris green used as an insecticide.

[February 28, 1901, became a law by constitutional limitation.]

The People of the State of California, represented in Senate and Assembly, do enact as follows:

SECTION 1. It shall be the duty of each and every manufacturer of paris green (commercial aceto-arsenite of copper) to be used as an insecticide within this State, and of every dealer in original packages of said paris green manufactured outside of this State, before the said paris green is offered or exposed for sale, or sold within this State as an insecticide, to submit to the Director of the California Agricultural Experiment Station at Berkeley, samples of said paris green, and a written or printed statement setting forth: first, the brands of said paris green to be sold, the number of pounds contained in each package in which it is put on the market for sale, the name or names of the manufacturers and the place of manufacturing the same; second, the statement shall set forth the amount of combined arsenic which the said paris green contains, and the statement so furnished shall be considered as constituting a guarantee to the purchaser

that every package of such paris green contains not less than the amount of combined arsenic set forth in the statement.

SEC. 2. Every purchaser of said paris green in original packages, which is manufactured outside of this State, who intends to sell or expose the same for sale, and every manufacturer of said paris green within this State, shall, after filing the statement above provided for, with the Director of the California Agricultural Experiment Station at Berkeley, receive from the said Director a certificate stating that he has complied with the foregoing statement, which certificate shall be furnished without charge therefor; said certificate when furnished shall authorize the party when receiving the same to deal in this State in the said paris green. Any person who fails to comply with the terms of section one of this Act shall not be entitled to such certificate and shall not be entitled to deal in said paris green within this State. Nothing in this section shall be construed as applying to retail dealers selling paris green which has already been labeled and guaranteed.

SEC. 3. Paris green, when sold, offered or exposed for sale, as an insecticide, in this State, shall contain at least fifty per centum of arsenious oxid, and shall not contain more than four per centum of the same in the uncombined state.

SEC. 4. The Director of the California State Agricultural Station at Berkeley shall examine or cause to be examined different brands of paris green sold, offered or exposed for sale within the State, and cause samples of the same to be analyzed, and shall report results of analyses forthwith to the Secretary of the State Board of Horticulture and to the party or parties submitting said samples, and such report shall be final as regards its quality.

SEC. 5. Any person or persons, firm, association, company or corporation violating any of the provisions of this Act, and any person who shall sell any package of paris green or any part thereof which has not been labeled as herein provided, shall be guilty of a misdemeanor, and shall be fined not less than fifty dollars nor more than two hundred dollars, together with the costs of the suit in an action caused to be brought by the State Board of Horticulture through its secretary in the name of the people of the State of California.

SEC. 6. The Attorney-General of the State of California is charged with the prosecution of all such suits.

SEC. 7. This Act shall take effect immediately.

Packages should be sent to the Agricultural Department at Berkeley for examination, and growers, when purchasing, should see that a certificate from the Director, Prof. E. W. Hilgard, accompanies the material.

Dealers in paris green would do well to correspond with the Director with regard to the sending of samples, as the Station takes its own specimens from trade lots whenever possible.

REPORTS AND BULLETINS AVAILABLE FOR DISTRIBUTION.

REPORTS.

1896. Report of the Viticultural Work during the seasons 1887–93, with data regarding the Vintages of 1894–95.

1897. Resistant Vines, their Selection, Adaptation, and Grafting. Appendix to Viticultural Report for 1896.

1898. Partial Report of Work of Agricultural Experiment Station for the years 1895–96 and 1896–97.

1900. Report of the Agricultural Experiment Station for the year 1897–98.

1902. Report of the Agricultural Experiment Station for 1898–1901.

BULLETINS.

No. 115. Remedies for Insect and Fungi. (Revised.)

121. The Conservation of Soil Moisture and Economy in the Use of Irrigation Water.

125. Australian Saltbush.

127. Bench-Grafting Resistant Vines.

128. Nature, Value, and Utilization of Alkali Lands.

129. Report of the Condition of Olive Culture in California.

131. The Phylloxera of the Vine.

132. Feeding of Farm Animals.

133. Tolerance of Alkali by Various Cultures.

134. Report of Condition of Vineyards in Portions of Santa Clara Valley.

135. The Potato-Worm in California.

136. Erinose of the Vine.

137. Pickling Ripe and Green Olives.

138. Citrus Fruit Culture.

139. Orange and Lemon Rot.

140. Lands of the Colorado Delta in Salton Basin, and Supplement.

141. Deciduous Fruits at Paso Robles.

142. Grasshoppers in California.

143. California Peach-Tree Borer.

144. The Peach-Worm.

145. The Red Spider of Citrus Trees.

146. New Methods of Grafting and Budding Vines.

147. Culture Work of the Substations.

148. Resistant Vines and their Hybrids.

149. California Sugar Industry.

150. The Value of Oak Leaves for Forage.

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